NBS TECHNICAL NOTE 1175

U.S. DEPARTMENT OF COMMERCE/National Bureau of Standards

Extension of a Reference Spectrophotometer into the Near Infrared

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Extension of a Reference Spectrophotometer into the Near Infrared

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The purpose of this paper is to document adaptation of an existing reference spectrophotometer to the near infrared. Its previous wavelength range was from approximately 200 to 800 nm. The present adaptation increases its wavelength range to 2500 nm. The hardware and software necessary to achieve this were implemented along with tests necessary to characterize the instrument when it is operated in the near infrared (800 to 2500 nm). The accuracy of the transmittance measurements ranges from approximately 0.0002 to 0.012 transmittance units depending on instrument configuration, wavelength, and the sample itself. Incidental to the success of this work was conversion to a dedicated microcomputer with interface boards. Many of the latter were designed at NBS.

Key words: lead sulfide detector; near infrared; photomultiplier; reference spectrophotometer; silicon photodiode; spectrophotometry; transmittance; wavelength.

1. Introduction

A high accuracy spectrophotometer [1], [2], [3][1] was adapted in order to perform measurements in the wavelength range from 800 to 2500 nm. We maintained a small systematic error. Many of the desirable features of the original design depend on using circular apertures instead of slits in the monochromator as well as off-axis parabolic mirrors to produce a collimated beam with no interreflection between sample and optics. It was decided to keep these features but in the adaptions some compromises had to be made. The bandpass was increased to approximately 6 nm from its previous value of approximately 0.75 to 1.5 nm. Since current practice is to use neutral filters (whose transmittance is not sensitive to bandpass) for transmittance standards, this compromise is not serious. Also, many absorption bands in the near infrared are broad. The sources and detectors which are currently available provide a smaller signal to noise ratio in the near IR than that which we have in the visible. This leads to larger random errors.

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[1]Figures in brackets indicate literature references at the end of this paper.

However, by repeating measurements and using the mean value, the standard deviation of the mean becomes less with the number of measurements. Care was taken in the choice of components and characterization of these components so that we can make measurements with a good estimate of the error in transmittance measurements.

2. Modifications for Extension into the Near Infrared

A schematic showing how the instrument is used over most of the wavelength range of interest is shown in figure 1. (Two other detectors used in the DC mode are for wavelengths from about 750 to 1100 nm, as will be described below.) Although many of the components shown in figure 1 have previously been described in other publications, they will be described in this paper briefly, and in some cases, the reader will be referred to other publications for details.

A. Sources and Source Optics

The He-Ne laser is used to define the optic axis, align the optics, and also to align the samples to be measured. Atomic line sources are used to calibrate the wavelength scale. A 500 watt coil filament lamp is used as an infrared source. It is aligned prior to measurements by rotation about a vertical axis so that the filaments approximate a spatially continuous source. A water-cooled jacket surrounds the lamp primarily to keep the surrounding space cool and reduce thermal effects on the rest of the apparatus. A 25.4 mm diameter flat mirror reflects the light beam onto a 51 mm diameter off-axis parabolic mirror of focal length 177 mm which collimates the light beam. Two lenses, one on either side of the chopper blade, focus the source on the chopper blade and then re-collimate the beam. These lenses are of high grade fused quartz whose index of refraction is constant with wavelength in the near infrared. The purpose of having an image of the filament on the chopper blade [4] is to provide illumination which increases and decreases uniformly in the sample compartment. Therefore, the use of two apertures for the linearity measurements will produce similar shaped waveforms with different amplitudes. These lenses are 37 mm in diameter with focal lengths of 200 mm. A Glan-Taylor prism polarizer produces a well-defined polarized beam. Normally, measurements are made with two polarizations--one with the electric vector parallel to the grating grooves (90°) and one with the electric vector perpendicular to the grating grooves (0°). A 51 mm square flat mirror then diverts the light onto a 51 mm diameter off-axis parabolic mirror of 195 mm focal length which produces an image of the source on the entrance slit of the predisperser.

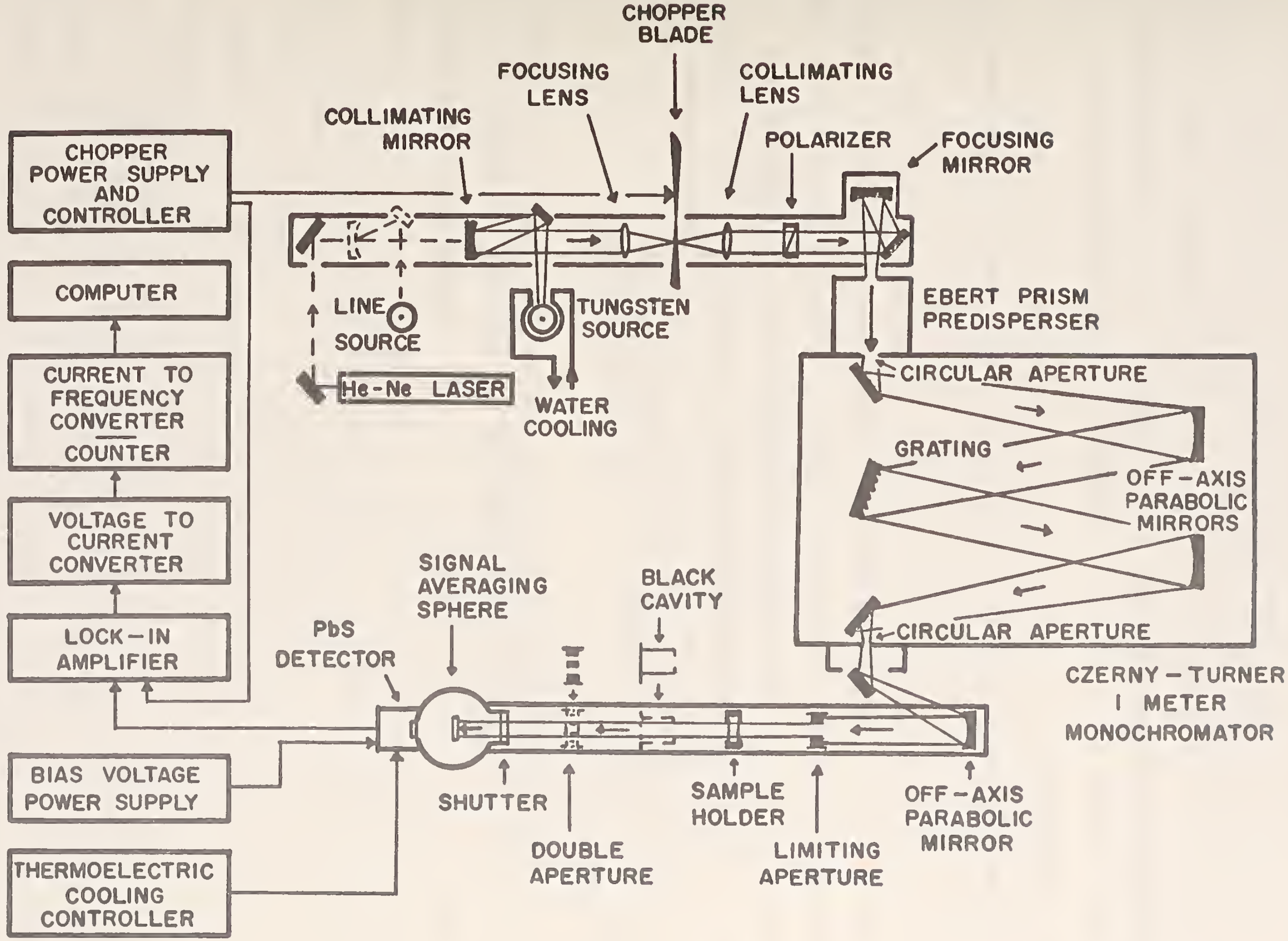

Figure 1. A schematic of the instrument with the PbS detector.

B. Wavelength Selection

An Ebert prism predisperser with f-number f/6 preselects the approximate wavelength band of interest. A one meter Czerny-Turner monochromator equipped with circular apertures at the entrance and exit ports and off-axis parabolic mirrors produces an approximate "point source" for the sample compartment optics. Its f-number is f/8.7. The grating is 102 mm by 102 mm with blaze wavelength at 800 nm and 150 grooves per mm. Normally, 1 mm diameter circular apertures are used in the monochromator which produce a bandpass of approximately 6 nm.

C. Sample Compartment

A 25.4 mm diameter flat mirror diverts the light onto a 51 mm diameter off-axis parabolic mirror of 195 mm focal length. These optics produce a collimated beam in the sample compartment of size 20 mm by 20 mm. A limiting aperture produces a beam of size and shape desired for a measurement. The sample holder is either a filter wheel or a sliding holder. The filter wheel allows up to 3 samples to be measured sequentially. The slide allows measurement of different size filters one at a time. Both holders are automated. A black cavity is used for measurement of the dark signal from the detector. A double aperture permits measurement of the linearity of the detection system [5].

D. Detectors and Spheres

The instrument sensitivity function, which includes the source, output efficiency of the optical system, and response of the detector, determines the useful wavelength range for a given detector. For our system, a photomultiplier with an extended S-20 cathode 50 mm in diameter will be used over the wavelength range of approximately 750 to 900 nm. A silicon photodiode can be used from approximately 900 to 1060 nm. A lead sulfide detector which is thermoelectrically cooled to -80 °C can be used from about 900 to 2500 nm. The spheres chosen for the PbS detector and the silicon photodiode are approximately 90 mm in diameter and have a diffusing target at their center. The sphere used for the photomultiplier does not have a target and is described in reference [6]. All three spheres have a pressed polytetrafluorethylene powder for their coatings [7]. The silicon photodiode (100 mm^2 surface area) and the photomultiplier are used in the direct current mode without the chopper and lock-in amplifier. The cooled PbS detector (10 mm by 10 mm) is used with the chopper and lock-in amplifier.

E. Electronics

The photoconductive PbS detector is connected to the preamplifier of a lock-in amplifier via the circuit shown in figure 2. The voltage output of the lock-in is applied across a thermally stable resistor of value 3.3 MΩ (voltage to current converter). The current in this circuit is measured by a current-to-frequency converter whose output pulses are counted by a counter which is read by a microcomputer. The lock-in amplifier is synchronized with a two-sector chopper blade with frequency of about 102 Hertz.

The photovoltaic silicon photodiode output current is measured directly by the current-to-frequency converter as is the output current from the photomultiplier.

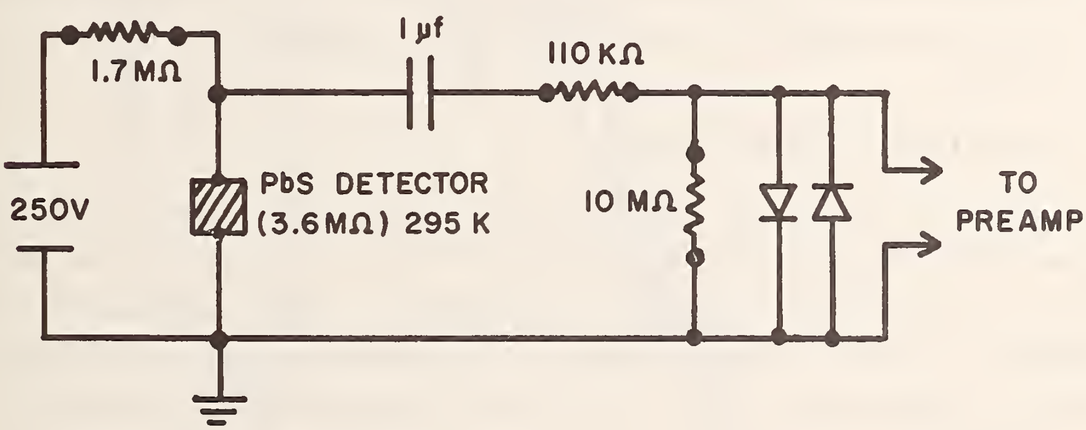

Figure 2. Photoconductive PbS detector circuitry.

F. Microcomputer and Interface Boards

The instrument is completely automated. This is achieved with a 64 K-byte memory dedicated microcomputer with an S-100 bus. A CRT display and printer are interfaced with the computer. Special relay boards, stepper motor control boards, and input/output boards enable automation of lock-in amplifier sensitivity setting, opening and closing of pneumatically controlled black cavity and shutter, and sample holder control, as well as setting of the wavelength of the monochromator and data acquisition.

3. Characterization

A. Instrument Sensitivity Function

The instrument sensitivity function is obtained by measuring the signal without a sample in the light beam. Since the spectrophotometer is a single beam instrument, this measurement as a function of wavelength reveals the wavelength region over which a given detector is useful. Since the centroid of the pass band also depends on this function, the function must be known for an accurate wavelength calibration. The instrument sensitivity functions using the cooled PbS detector, the silicon photodiode, and the extended S-20 photomultiplier are shown in figures 3, 4, and 5, respectively. The predominant features of the function for the PbS detector are caused by a decreasing sensitivity of the detector itself at long wavelengths, the wavelength dependence of the efficiency of the grating blazed at 800 nm, and absorption by the mirror optics near 800 nm. The silicon photodiode is similarly affected except that its responsivity drops at much shorter wavelengths. The photomultiplier responsivity is essentially zero at 950 nm.

B. Stability--Drift and Noise

The stability of the source-detector combinations using the 500 watt source and three detectors was determined by alternately measuring the signal and dark signal at equal time intervals for 30 minutes. These measurements determine the system drift which can be eliminated from measurements by taking data in such a fashion as to determine the drift each time a transmittance measurement is made. Superimposed on the drift are fluctuations which must be regarded as noise and cannot be eliminated from a measurement--thus leading to an uncertainty. Typical curves illustrating these two effects are shown in figures 6, 7, and 8 for the three detectors along with values of the drift and coefficient of variation of the residual noise $\frac{dI}{I}$ for a 30-minute period.

We see that the drift is fairly linear and can be taken into account. The noise depends on the signal level and is given only for those tests used to obtain the figure. The noise for other signal levels for the PbS detector is given in table 1.

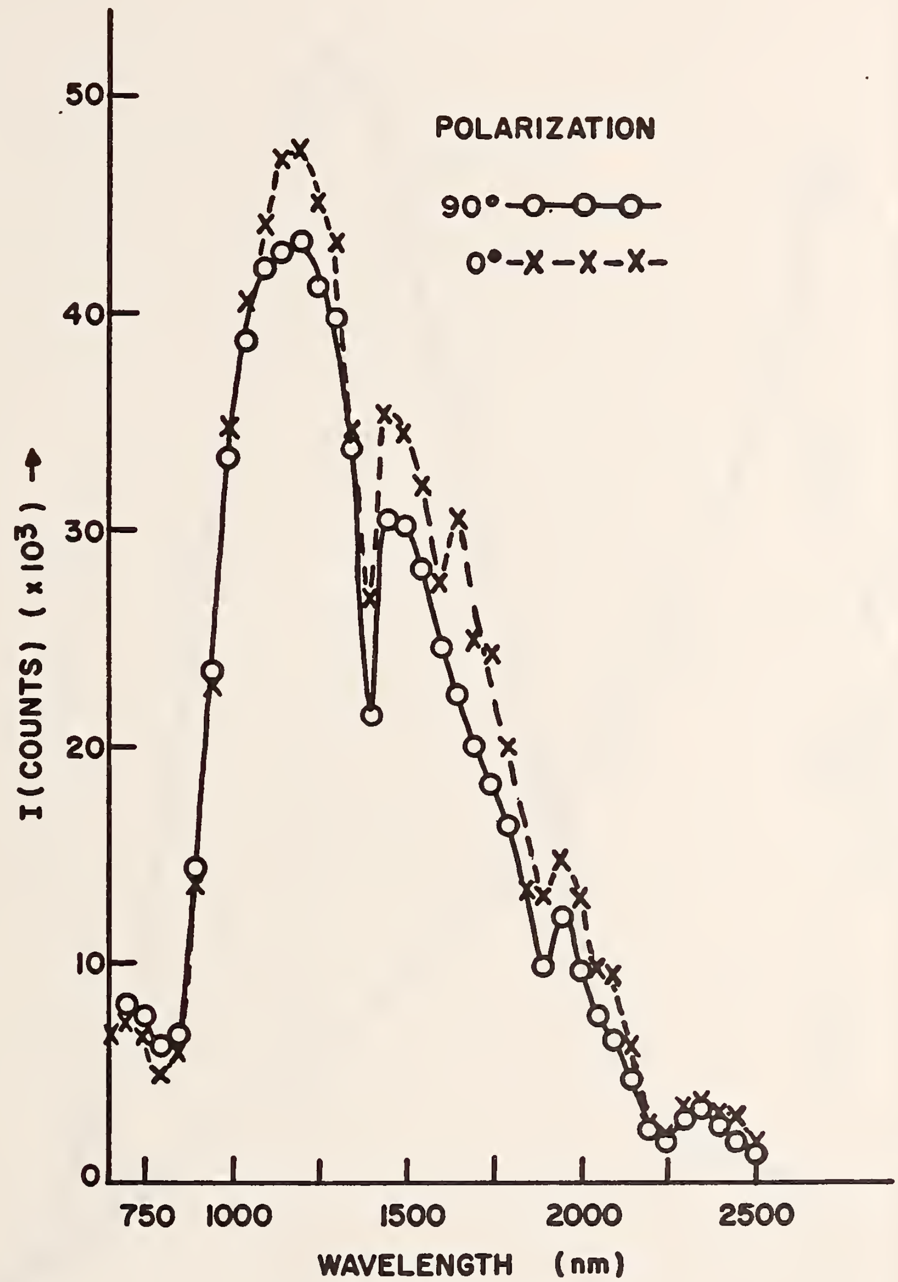

Figure 3. Instrument sensitivity function using the cooled PbS detector. All counts in this and following figures refer to accumulation over a 10-second time interval. The maximum count level in this figure is 50,000.

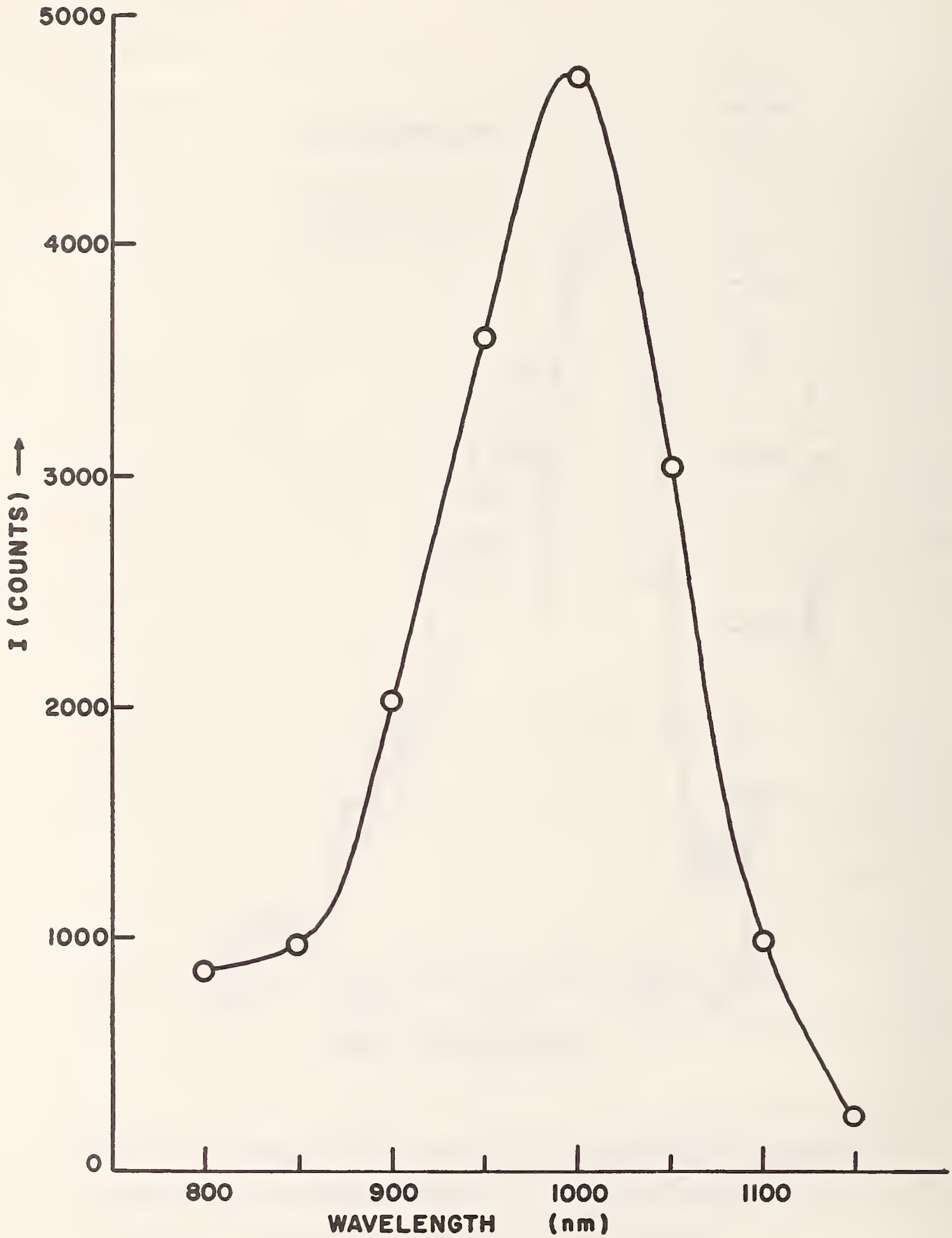

Figure 4. Instrument sensitivity function using the silicon photodiode.

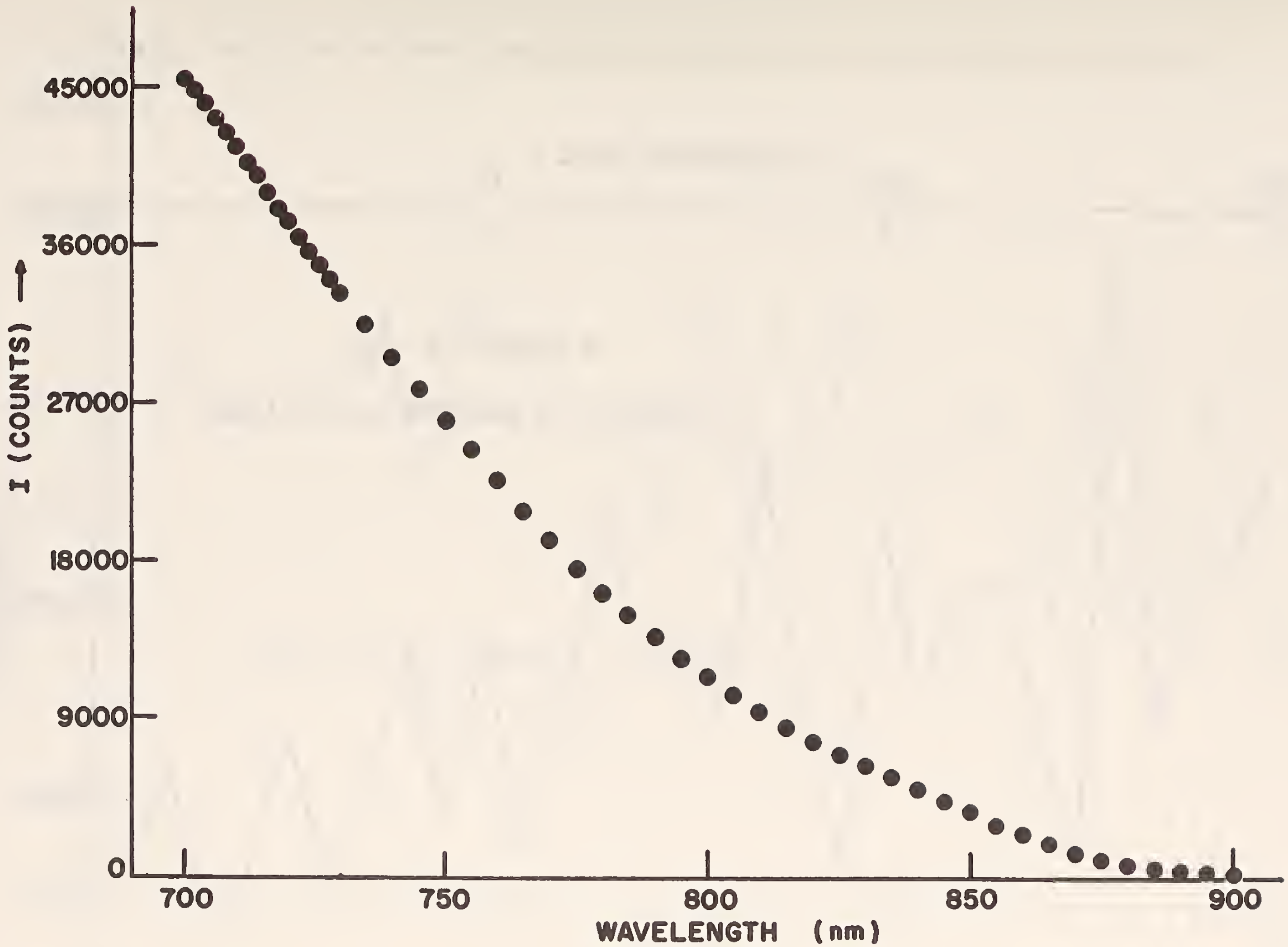

Figure 5. Instrument sensitivity function using the extended S-20 photomultiplier tube.

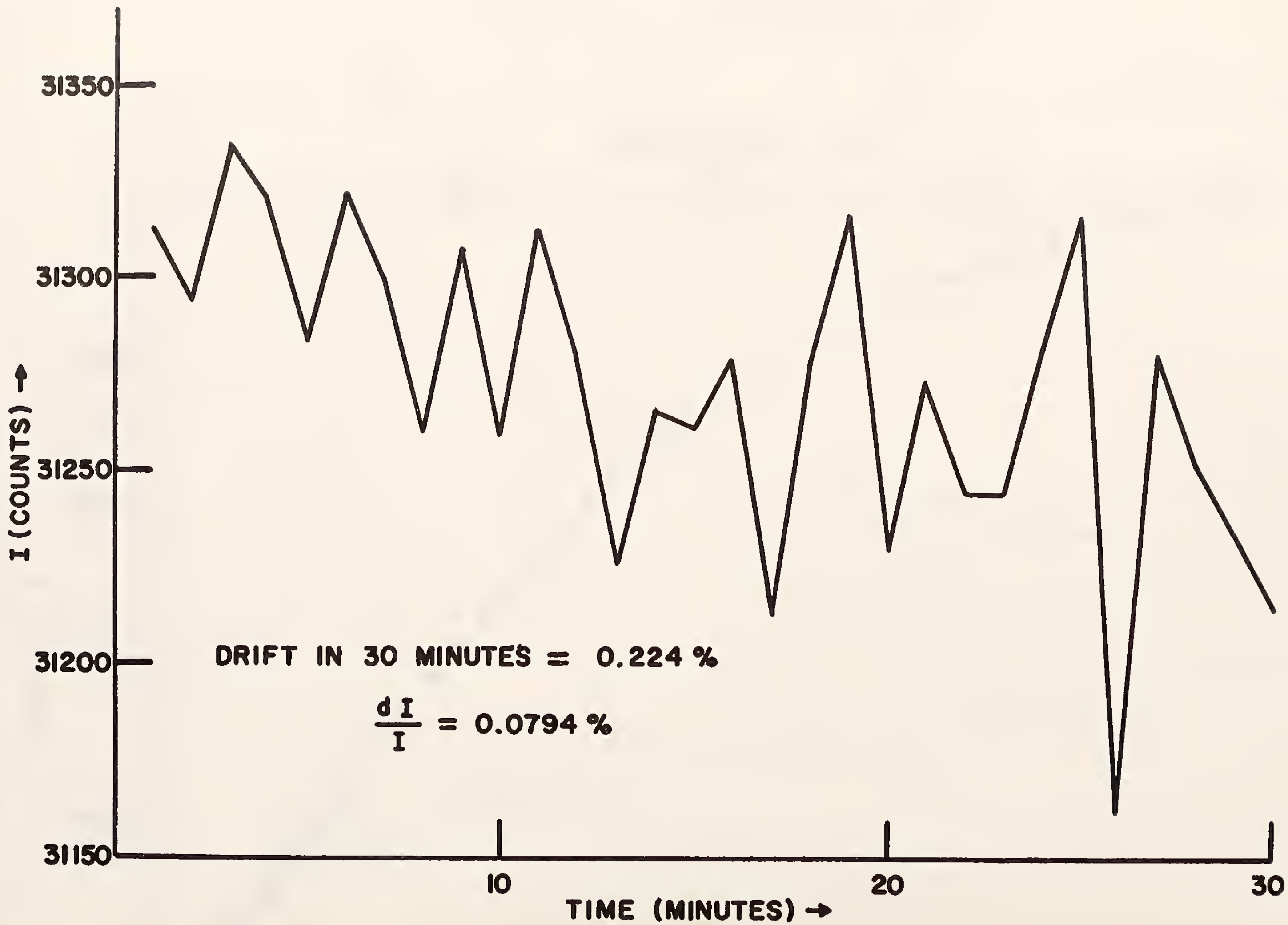

Figure 6. Drift and standard deviation of the noise for the cooled PbS detector.

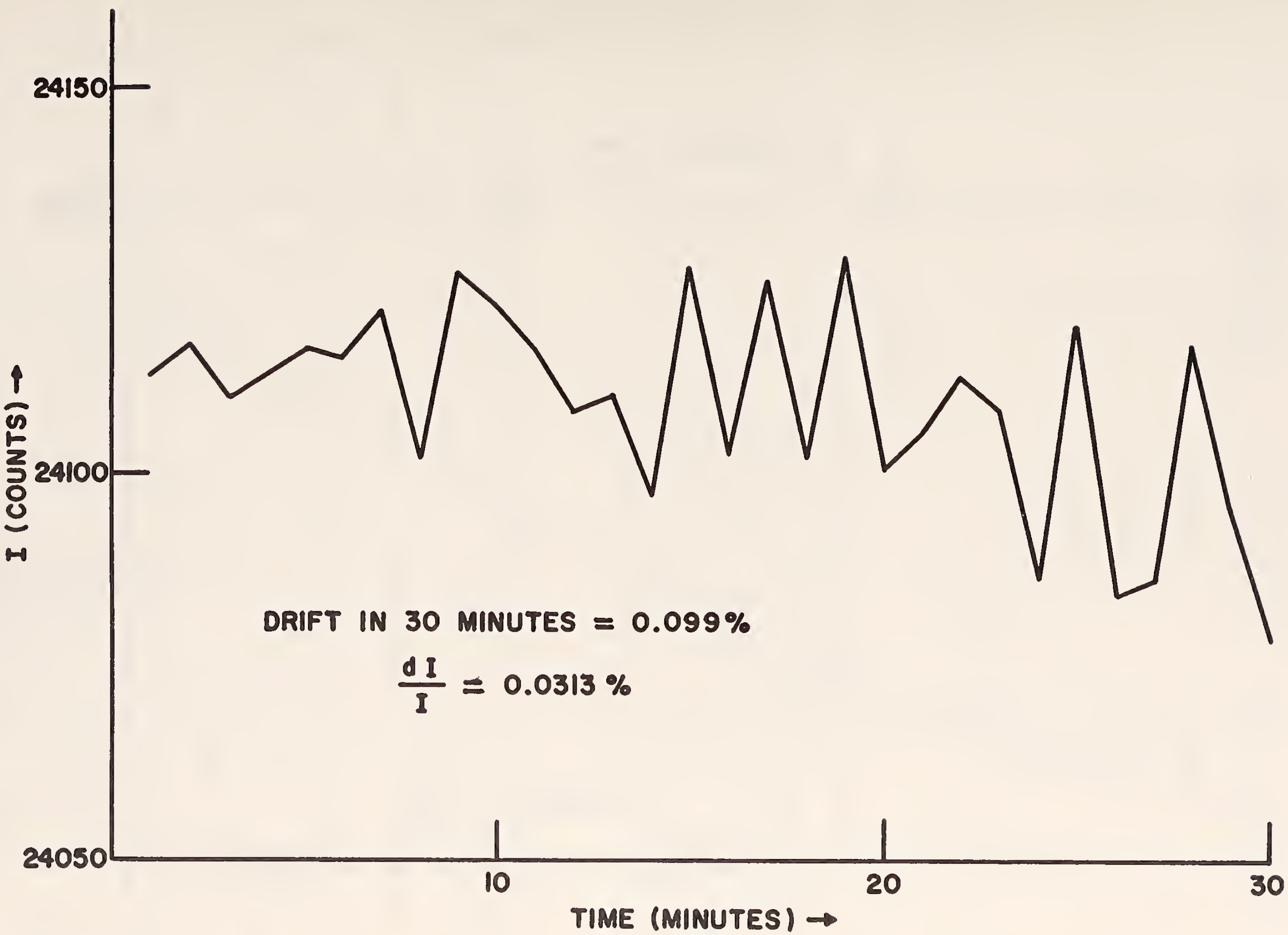

Figure 7. Drift and standard deviation of the noise for the silicon photodiode.

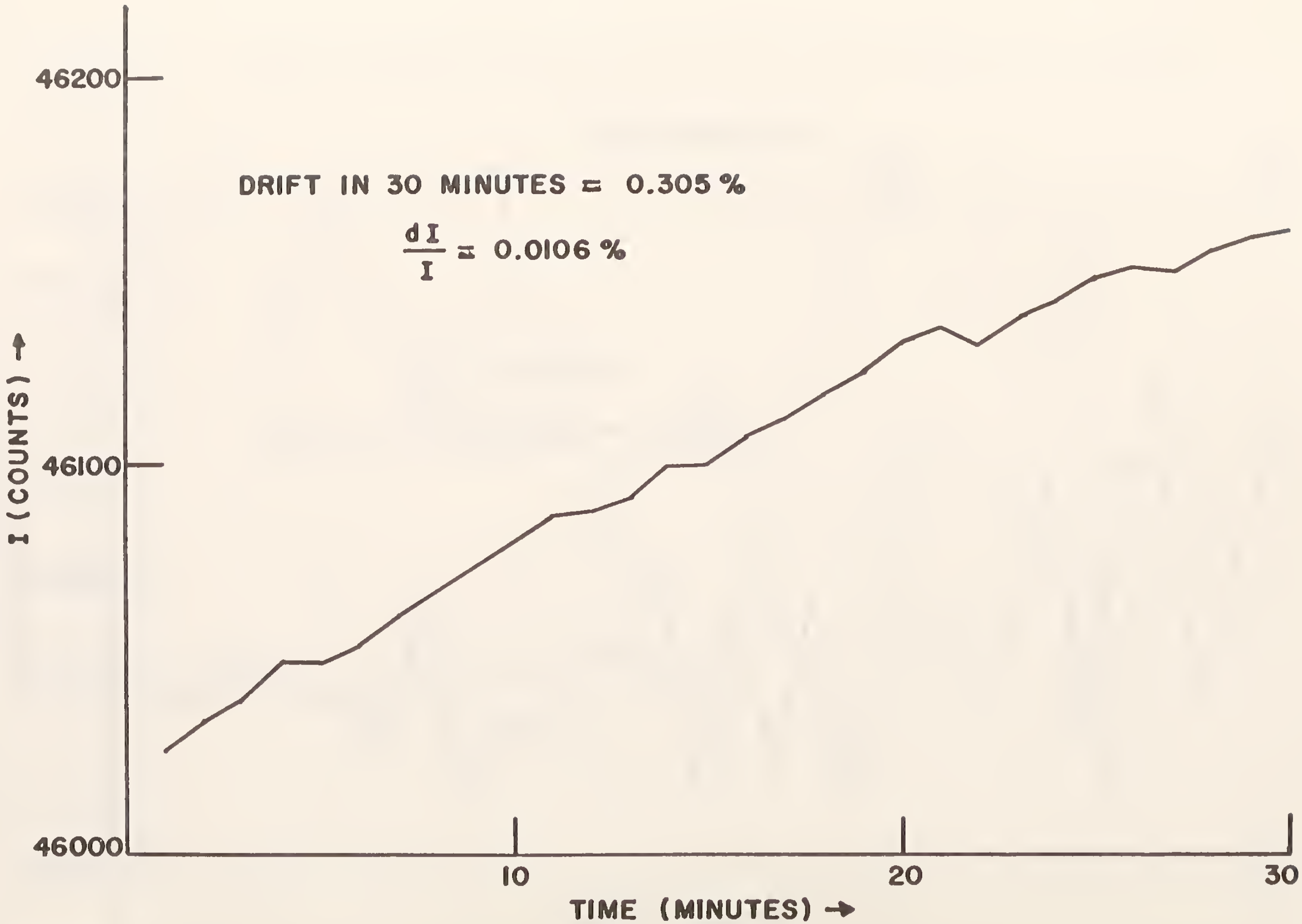

Figure 8. Drift and standard deviation of the noise for the extended S-20 photomultiplier tube.

Table 1. Drift and noise using the PbS detector and the lock-in amplifier at several sensitivity settings.

Lock-in Amplifier Sensitivity	Average Drift for 30 min (%)	$\frac{dI}{I}$ (%)
1 mV	0.5189	0.4752
2 mV	0.6988	0.2985
5 mV	0.5146	0.1576
10 mV	0.2241	0.0794

C. Uniformity of Receivers

Our receivers consist of an averaging sphere and detector. Since the detectors are non-uniform across their surface, a sphere tends to average this effect. Non-uniformity of the receiver must be taken into account because when a sample which is slightly wedge shaped is inserted into the light beam it deflects the beam slightly. Even if the surfaces of the sample are plane parallel and it is inserted into the light beam at an angle, the sample will also deflect the beam.

Tests carried out on the averaging sphere used for the photomultiplier tube have been discussed previously [6], [3]. Results of those tests indicate an efficiency of approximately 50 percent and that a beam deflection of 1 mm (a large deflection) would cause an error of approximately 0.01 percent.

The type of sphere used for the photovoltaic silicon detector and the photoconductive PbS detector has been shown to have a high efficiency if the detector is properly coupled to the sphere [8]. The uniformity was measured by moving the sphere and detector ±0.5, ±1.0, and ±1.5 mm about the central position both horizontally and vertically. (See figures 9 and 10.) Since the differences are small, the noise (the error bars indicate 3 standard deviations) obscures any real effect. However, there seems to be a trend in the horizontal scan. The scans were made in a sequence such that the drift in the data was eliminated, i.e., the scans were made at equal time intervals in the sequence 0, .5, 1, 1.5, 1.5, 1.0, 0.5, 0 in positive and negative directions and the resulting data averaged, assuming a linear drift.

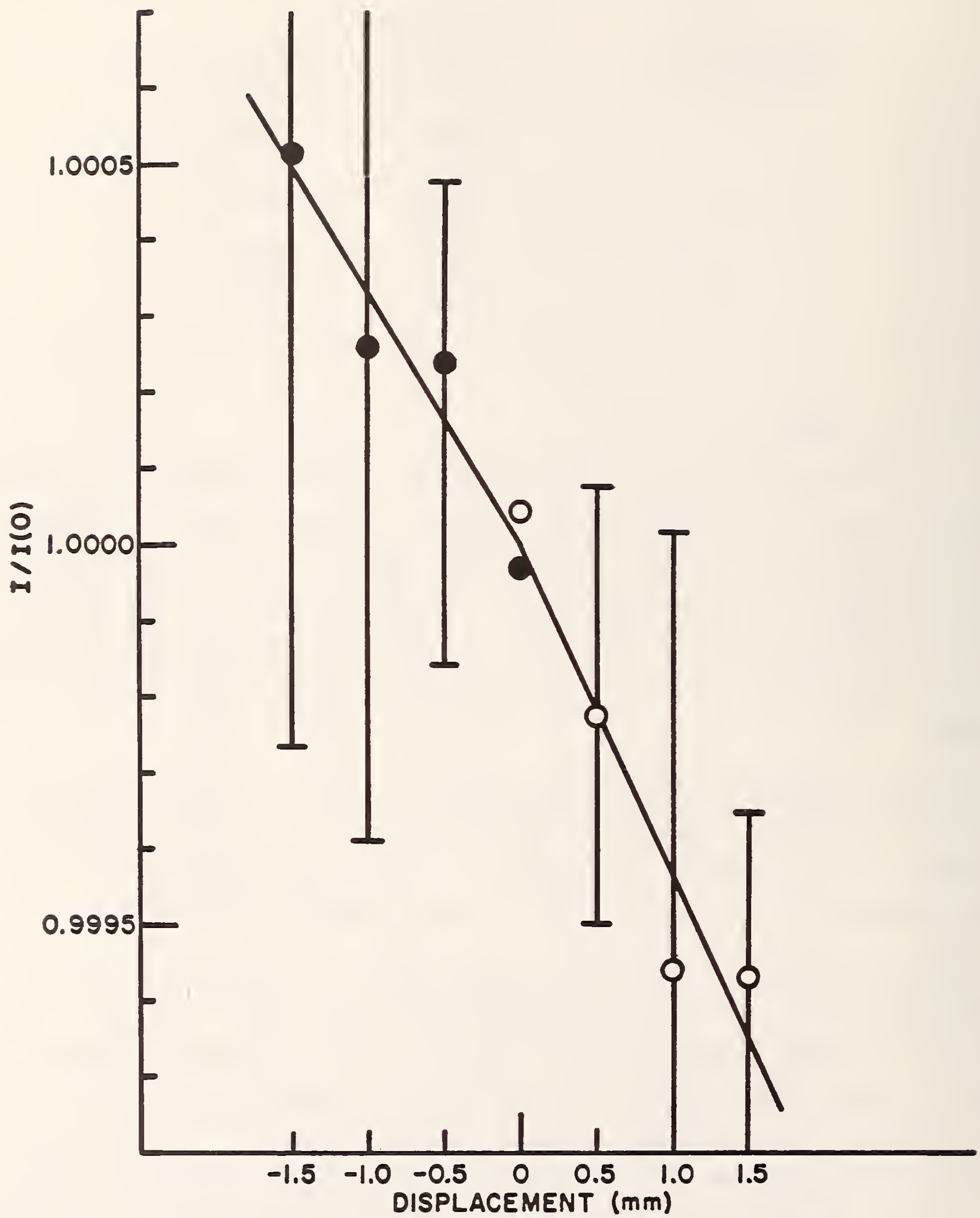

Figure 9. Horizontal uniformity of the PbS detector-averaging sphere combination.

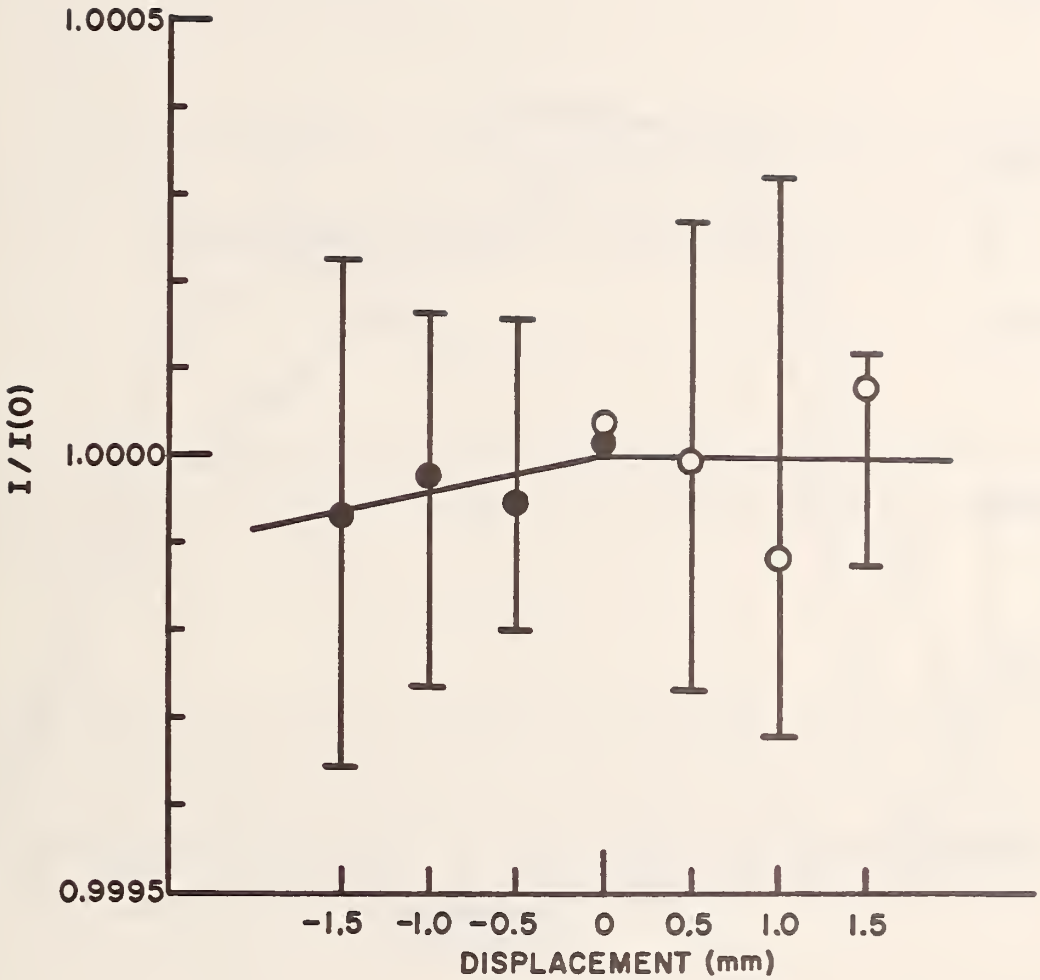

Figure 10. Vertical uniformity of the PbS detector-averaging sphere combination.

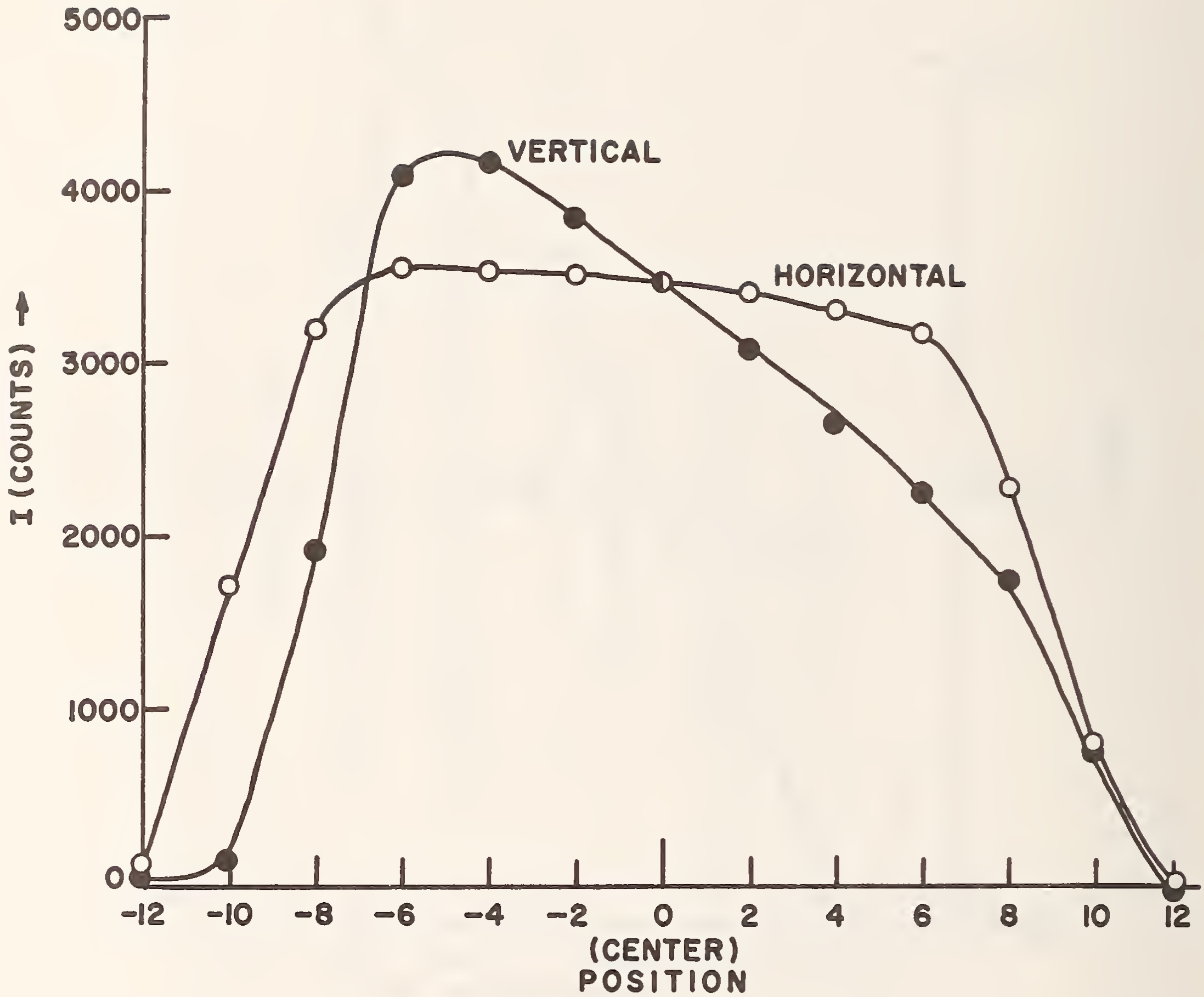

Figure 11. Uniformity of the light beam in the sample compartment. The abscissa refers to positions in units of millimeters.

D. Uniformity of Light Beam

The uniformity of the light beam is not very critical since most samples to be measured must be quite uniform to qualify as a transmittance standard. A 5 mm diameter aperture was scanned horizontally and vertically across the light beam. Typical results are shown in figure 11. It is seen that in the worst case the signal differs by 40 percent from the signal obtained at the center position for the useful portion of the beam.

E. Linearity

All spectrophotometers are subject to a non-linearity of the photometric scale to some degree. This non-linearity may be expressed as an additive correction, ΔT, to the measured transmittance, T_a, so that the real transmittance, T, is

$$T = T_a + \Delta T.$$

The quantity, ΔT, was determined by using the double aperture method as described in reference [5]. If the signal current for the detectors can be expressed by the equation

$$I(\phi) = \eta G(\phi)\phi$$

then the relevant derivations in reference [5] apply here. ϕ is the incident flux, η is the quantum efficiency, and G is the effective gain. This is true for the PbS detector because the signal current may be expressed in terms of the gain of the lock-in amplifier, $g(\phi)$, the signal voltage from the PbS detector, V_s, and the voltage to current resistance, R_{VI}, [9] such that

$$\begin{aligned} I(\phi) &= \frac{g(\phi)V_s}{R_{VI}} \\ &= \frac{g(\phi)}{R_{VI}} \left[\frac{E\ R_c R_L}{(R_c+R_L)^2} \phi\eta A \frac{\tau}{n} \left(\frac{1}{1+\omega^2\tau^2} \right)^{\frac{1}{2}} \right] \\ &\equiv \eta G(\phi)\phi \end{aligned}$$

where

E = bias voltage (250 V in figure 2)

R_c = resistance of the PbS detector (3.6 MΩ in figure 2)

R_L = load resistor (1.7 MΩ in figure 2)

ϕ = radiant flux

η = quantum efficiency of the PbS detector

A = cross sectional area of PbS detector perpendicular to current flow

τ = lifetime of charge carrier in PbS detector

n = number of free charge carriers in PbS detector

ω = angular frequency of modulation of the chopper.

The signal current I for the silicon photodiode can be expressed by the following expression [10]

$$I(\phi) = \phi Q(\phi)$$

where $Q(\phi)$ is the external quantum efficiency. The external quantum efficiency is [10]

$$Q(\phi) = (1-\rho)\ \eta F(\phi)$$

where ρ is the reflectance of the photodiode, and $F(\phi)$ is the collection efficiency for our geometry. Thus, the signal current for the silicon photodiode can also be expressed as

$$I(\phi) = \eta G(\phi)\phi.$$

The linearity correction ΔT for the photomultiplier tube, PbS detector, and silicon photodiodes and the standard deviation of ΔT, $\delta(\Delta T)$ are listed below for transmittance T. The scale indicated is that for the current-to-frequency converter, and the sensitivity indicated for the PbS detector is the lock-in-amplifier sensitivity setting. We found that the useful sensitivity settings for the lock-in amplifier range from 1 to 50 mV.

	Photomultiplier 3×10^{-7} amp scale (Measured at 850 nm)		PbS 3×10^{-6} amp scale 10 mV sensitivity (Measured at 1250 nm)		Si photodiode 3×10^{-8} amp scale (Measured at 1060 nm)	
T	ΔT $\times 10^{-4}$	$\delta(\Delta T)$ $\times 10^{-6}$	ΔT $\times 10^{-4}$	$\delta(\Delta T)$ $\times 10^{-4}$	ΔT $\times 10^{-4}$	$\delta(\Delta T)$ $\times 10^{-4}$
0.1	1.10	2.03	-0.41	0.65	0.97	0.71
0.2	2.05	3.10	-0.40	0.90	1.28	1.00
0.3	2.80	3.98	-0.10	0.92	1.12	1.09
0.4	3.32	5.13	0.37	0.92	0.63	1.18
0.5	3.59	6.49	0.90	1.06	-0.02	1.41
0.6	3.58	7.61	1.35	1.31	-0.07	1.68
0.7	3.24	8.01	1.61	1.47	-1.15	1.84
0.8	2.55	7.20	1.55	1.40	-1.30	1.70
0.9	1.48	4.68	1.06	0.96	-0.98	1.14
1.0	0.00	0.00	0.00	0.00	0.00	0.00

It is seen that only for the photomultiplier tube is the standard deviation of ΔT, $\delta(\Delta T)$, significantly less than ΔT. For all three detectors, we regard $\delta(\Delta T)$ as a systematic error in the measurement of transmittance, T, which will vary depending on detector and sensitivity scale used.

F. Stray Radiant Energy

New methods for measuring stray radiant energy and the stray light ratio have recently been published [11], [12]. The stray radiant energy is defined by ASTM Method E387 [13]. It generally underestimates the effect of stray light on a spectrophotometric measurement. The stray light ratio as defined by Kaye sometimes allows a correction to be made. However, for a general characterization of our instrument, we chose to measure stray radiant energy using filters and a liquid, whose properties are well known, to obtain order of magnitude estimates of stray light. If we ever desire to make measurements where the stray light will become a problem, we will attempt, using appropriate blocking filters, to measure the stray light ratio. This seems reasonable, since as Kaye points out, the sample itself can influence the stray light ratio. Further, except for the

extended S-20 photomultiplier, our measurements of stray light are noise-limited. That is, the mean of 100 measurements of stray radiant energy expressed as apparent transmittance is usually about the same magnitude as the standard error (standard deviation of the mean) for that measurement.

Samples of chloroform, selenium filter, germanium windows, and silicon wafers have been shown to be useful for measuring stray radiant energy [14]. Also, two broad-band interference filters which transmit almost the whole visible spectrum were used to estimate stray light for the silicon photodiode and the photomultiplier.

The silicon wafers cut off wavelengths below about 900 nm and transmit more than 52 percent at wavelengths out to 2500 nm. The selenium glass has a cut-off at approximately 800 nm and transmits approximately 88 percent out to 2500 nm. The 4 mm germanium window starts cutting off at approximately 1950 nm and transmits approximately 46 percent out to 2500 nm. The combination of 3 mm and 4 mm germanium windows transmits approximately 27 percent between 1950 and 2500 nm. The first interference filter (no. 1) cuts off at about 700 nm and transmits more than 70 percent over most of the visible spectrum. The other interference filter (no. 2) cuts off at about 850 nm and has a transmittance exceeding 80 percent over the visible spectrum and has a low transmittance in the near infrared. Chloroform has a strong absorption band at about 1690 nm.

Consequently, the silicon, germanium, and silicon filters test for long wavelength stray radiant energy. The interference filters in combination test for short wavelength stray radiant energy and the chloroform tests for both short and long wavelength stray radiant energy.

(1) Photoconductive PbS Detector

Two measurements were made at 1690 nm with a 10 mm thick cuvette containing chloroform. The measurements were repeated 100 times with a 10-second integration time by first measuring the dark signal and then the signal with the chloroform in the beam. The clear space signal was measured at the beginning and end of each 100 measurements. The results are shown below as apparent transmittance, τ_a.

	Approximate Wavelength	Mean τ_a ± Standard Error
Run 1	1690 nm	$3.76 \times 10^{-4} \pm 0.92 \times 10^{-4}$
Run 2	1690 nm	$4.06 \times 10^{-4} \pm 0.91 \times 10^{-4}$.

If we take 3 standard errors to be the uncertainty of the measurement which is less than the mean τ_a, the stray light is of the order of 10^{-4}.

In a similar manner, a 3 mm thick germanium window was placed in the beam, and then the combination of 3 mm and 4 mm windows was placed in the beam for 100 measurements each. The results follow:

Approximate Wavelength	Sample	Mean τ_a ± Standard Error
900 nm	3 mm Ge	$4.85 \times 10^{-5} \pm 7.26 \times 10^{-5}$
900 nm	3 mm Ge + 4 mm Ge	$8.45 \times 10^{-5} \pm 7.72 \times 10^{-5}$
1100 nm	3 mm Ge	$2.23 \times 10^{-6} \pm 2.01 \times 10^{-5}$
1100 nm	3 mm Ge + 4 mm Ge	$1.53 \times 10^{-5} \pm 2.22 \times 10^{-5}$
1500 nm	3 mm Ge	$3.67 \times 10^{-5} \pm 3.30 \times 10^{-5}$
1500 nm	3 mm Ge + 4 mm Ge	$-2.79 \times 10^{-7} \pm 3.41 \times 10^{-5}$

Again we see that, taking 3 standard errors as the error in the measurement, the stray light is of the order of 10^{-4} or less.

(2) Photovoltaic Silicon Photodiode

Two silicon wafers, two germanium windows, and two interference filters (the latter transmit the visible spectrum almost entirely) were used to obtain estimates of the stray light for this detector. The interference filters are each known to transmit approximately one percent at 900 nm. Consequently, neglecting interreflections (a conservative assumption) the combination should transmit approximately 10^{-4} of the incident radiation at 900 nm. The results are:

Approximate Wavelength	Sample	Mean τ_a ± Standard Error
850 nm	1 Silicon Wafer	$1.18 \times 10^{-4} \pm 8.37 \times 10^{-5}$
850 nm	2 Silicon Wafers	$-2.02 \times 10^{-5} \pm 8.92 \times 10^{-5}$
900 nm	3 mm Germanium	$-1.20 \times 10^{-4} \pm 3.91 \times 10^{-5}$
900 nm	3 mm Ge + 4 mm Ge	$-2.01 \times 10^{-4} \pm 4.11 \times 10^{-5}$
900 nm	Interference Filter No. 1	$1.017 \times 10^{-2} \pm 3.443 \times 10^{-5}$
900 nm	Interference Filter No. 2	$9.138 \times 10^{-3} \pm 4.890 \times 10^{-5}$
900 nm	Combination of Filters No. 1 and No. 2	$2.568 \times 10^{-4} \pm 3.990 \times 10^{-5}$

We again see that we are noise limited, and the stray radiant energy measured with the Si wafers and the Ge windows is of the order of 10^{-4} or less. The interference filters in combination should transmit on the order of 9×10^{-5} whereas we measure a higher amount by 1.6×10^{-4} with three standard errors of 1.2×10^{-4} so that again the stray radiant energy is of the order of 10^{-4} or less.

(3) Extended S-20 Photomultiplier

Stray radiant energy at 725 nm as measured with the selenium filter had a mean τ_a of 1.44×10^{-5} with a standard error of 6.37×10^{-7}. The stray radiant energy from long wavelengths was also measured with the germanium filters with the results:

Approximate Wavelength	Sample	Mean τ_a ± Standard Error
900 nm	3 mm Ge	$4.68 \times 10^{-5} \pm 8.41 \times 10^{-7}$
900 nm	3 mm Ge + 4 mm Ge	$1.37 \times 10^{-7} \pm 7.13 \times 10^{-8}$

These numbers are very small since the detector is not sensitive to wavelengths above 950 nm. However, this detector is very sensitive to visible radiation, and it was necessary to use a blocking filter to absorb wavelengths below 750 nm to obtain low stray radiant energy from the visible at 900 nm. A stray radiant energy of 0.5 percent was observed without the blocking filter. The results with and without the blocking filter are reported for illustration.

Without Blocking Filter

Approximate Wavelength	Sample	Mean τ_a ± Standard Error
900 nm	Interference Filter 1	$1.671 \times 10^{-2} \pm 1.746 \times 10^{-6}$
900 nm	Interference Filter 2	$1.762 \times 10^{-2} \pm 1.895 \times 10^{-6}$
900 nm	Combination of 1 and 2	$5.240 \times 10^{-3} \pm 4.285 \times 10^{-7}$

With Blocking Filter

Approximate Wavelength	Sample	Mean τ_a ± Standard Error
900 nm	Interference Filter 1	$1.039 \times 10^{-2} \pm 5.840 \times 10^{-7}$
900 nm	Interference Filter 2	$9.063 \times 10^{-3} \pm 8.966 \times 10^{-7}$
900 nm	Combination of 1 and 2	$9.346 \times 10^{-5} \pm 8.881 \times 10^{-7}$

The measurements of the individual interference filters show transmittances which, when multiplied together, predict a transmittance, neglecting interreflections, for the combination of 9.42×10^{-5}. Comparison with the combination of filters 1 and 2 leads one to predict that the stray radiant energy is 10^{-6} or less when using the blocking filter.

G. Wavelength Calibration

The dial reading of the spectrophotometer on a counter (CN) may not indicate the true wavelength. We account for this fact by calibrating the dial to give a wavelength correction, $\Delta\lambda$,

$$\Delta\lambda = \lambda_{CN} - \lambda_{TRUE}$$

where λ_{CN} is the dial reading and λ_{TRUE} is the published wavelength for a given atomic line. The atomic lines that were used are given in table 2. We scanned the instrument across the lines and chose the peak wavelength as λ_{CN}. Using the photomultiplier and measuring the Rb lines we showed that our entrance and exit apertures are symmetrical and the half-height bandpass is approximately 5.5 nm.

Table 2. The elements and wavelengths of the atomic lines used for the wavelength calibration and the published values for the minima of the absorption bands.

Element or Chemical	Wavelength (nm)
Rb	780.02
Rb	794.76
Hg	1013.98
Hg	1128.70
Hg	1529.52
Hg	1692.1
Hg	1970.1
1,2,4-trichlorobenzene	2152.6
1,2,4-trichlorobenzene	2437.4

By using these lines, figure 12 was obtained by plotting the wavelength correction, $\Delta\lambda$, as a function of wavelength λ, and fitting a straight line through the resulting data using the method of least squares.

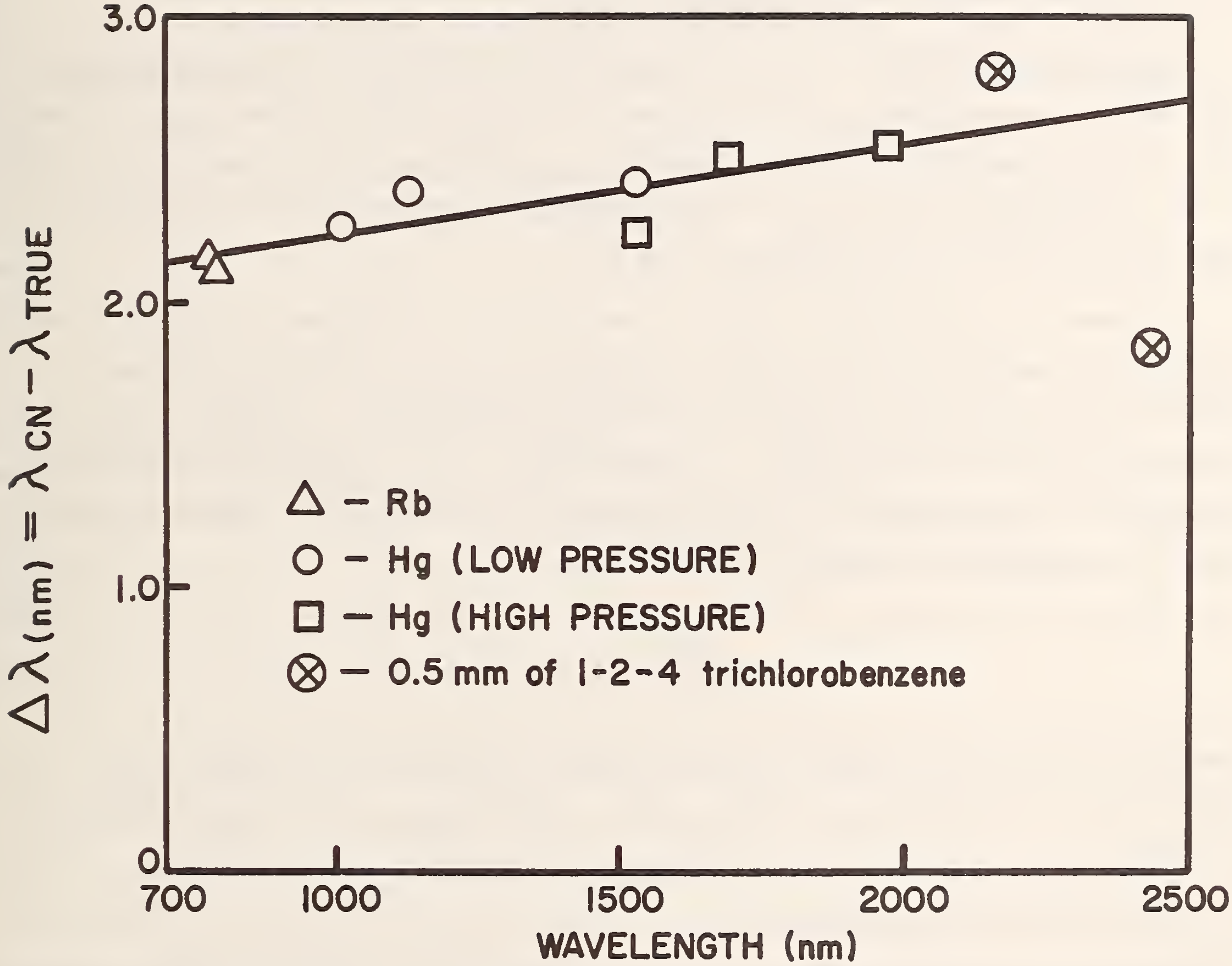

Figure 12. Wavelength correction curve.

Due to the fact that our system has a low sensitivity near 2500 nm and the atomic lines that we attempted to measure were relatively weak, we did not obtain any data for atomic lines beyond 1970.1 nm. There are some absorption bands in 1,2,4-trichlorobenzene whose wavelengths have been published [15]. We chose to measure two of these that are relatively symmetrical, and thus insensitive to bandpass. The uncertainty in these published values is given in reference [15] as ±1 nm. The least squares fit of the atomic lines falls within 1 nm of the measured minima of the absorption bands.

Repeated measurements on the Hg lines show the noise in the measurements obtained by scanning the instrument across the atomic lines. The range of this error is approximately 0.15 nm. Therefore, we assign a total uncertainty as the sum of a systematic error of 0.18 (the difference obtained with two types of lamps) plus 0.15/2 or approximately 0.26 nm.

If there is a substantial rate of change of the instrument sensitivity function with wavelength, the effect would be to cause the actual passband centroid to be shifted away from the geometrical passband. In such a case, further corrections must be made. In particular, for a triangular geometrical passband the displacement dλ of the passband centroid from the center of the geometrical passband is given by [16]

$$d\lambda = \frac{aw^2}{6}$$

where a is the slope of the instrument sensitivity curve normalized at the center of the triangle and w is the width at half-height of the geometrical passband.

4. Transmittance Measurements

We have shown above that the drift with time of the signals obtained with the detectors is essentially linear over a period of time of 10 to 20 minutes--the time necessary to make transmittance measurements. This means that we can use a previously published method for taking and analyzing the data [3]. Our automatic filter holders accommodate one to three filters at a time. We devised a method of taking the data in a symmetrical fashion such that four measurements are made for each filter, the clear space or 100 percent signal is measured five times, and dark signals are interspersed between. Each reading takes 20 seconds--a 10 second wait and then a 10 second integration time. Differences from previous

data-taking techniques are required primarily because of the large dynamic range of the instrument sensitivity functions and the noise at low signal levels especially for the PbS detector. In order to conserve flux levels at their highest possible values, we chose to eliminate one Glan-Taylor polarizer and to adjust automatically the sensitivity scale on the lock-in amplifier at each wavelength. This adjustment is made by a combination of software in the computer and hardware in the lock-in amplifier.

Previous estimates for the systematic error for this instrument over the wavelength range 200 to 800 nm are approximately 0.0001 transmittance units for a filter having a transmittance of 0.1 to 0.92. The random error expressed as the standard error for four measurements varied from approximately 0.00003 to 0.0002 depending on the level of transmittance. Lower transmittances were measured using a step-down technique [1] with a corresponding propagation of errors.

The uncertainties in transmittance in the near infrared vary by two orders of magnitude depending on the wavelength, filter, and the detector used. It would be possible to construct tables estimating the errors for all wavelengths and transmittances. However, the number of measurements would be very large, and the measurements would have to be repeated for a meaningful calibration. Consequently, we chose to sample the possibilities, and it is possible to give order of magnitude estimates for any future measurements.

The linearity was measured for the photomultiplier, silicon photodiode, and lead sulfide detectors. The uncertainties in these measurements are regarded as systematic errors. The standard error in the non-linearity for the photomultiplier is sufficiently small so that the systematic error estimate remains as approximately 0.0001 transmittance units. The standard error in the non-linearity for the silicon photodiode is about 1.4×10^{-4} transmittance units. We therefore estimate the systematic error to be 0.0001 plus 3 times 1.4×10^{-4} or about 0.0005 transmittance units. Non-linearity measurements with the PbS using the 10 mV and 2 mV scales have standard errors ranging from 0.00014 to 0.0007, respectively. Consequently, we have systematic errors ranging from 0.0005 to 0.003.

The random errors are determined by repeated measurements. The standard error for 4 measurements will vary from about 0.00003 for the photomultiplier and low transmittance filter to 0.003 for the PbS detector and medium transmittance filter at the extreme wavelength of 2500 nm where the instrument sensitivity function is small.

The total uncertainty is usually conservatively estimated as the systematic error plus three times the standard error. This gives estimates ranging from approximately 0.0002 to 0.012 transmittance units depending on the apparatus used, wavelength, and transmittance of the filter to be measured.

We have used state-of-the-art equipment to extend the wavelength range of this spectrophotometer into the near infrared. We believe that the instrument will provide a valuable measurement capability for the National Bureau of Standards.

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The purpose of this paper is to document adaptation of an existing reference spectrophotometer to the near infrared. Its previous wavelength range was from approximately 200 to 800 nm. The present adaptation increases its wavelength range to 2500 nm. The hardware and software necessary to achieve this were implemented along with tests necessary to characterize the instrument when it is operated in the near infrared (800 to 2500 nm). The accuracy of the transmittance measurements ranges from approximately 0.0002 to 0.012 transmittance units depending on instrument configuration, wavelength, and the sample itself. Incidental to the success of this work was conversion to a dedicated microcomputer with interface boards. Many of the latter were designed at NBS.

12. KEY WORDS (Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons)

lead sulfide detector; near infrared; photomultiplier; reference spectrophotometer; silicon photodiode; spectrophotometry; transmittance; wavelength.

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